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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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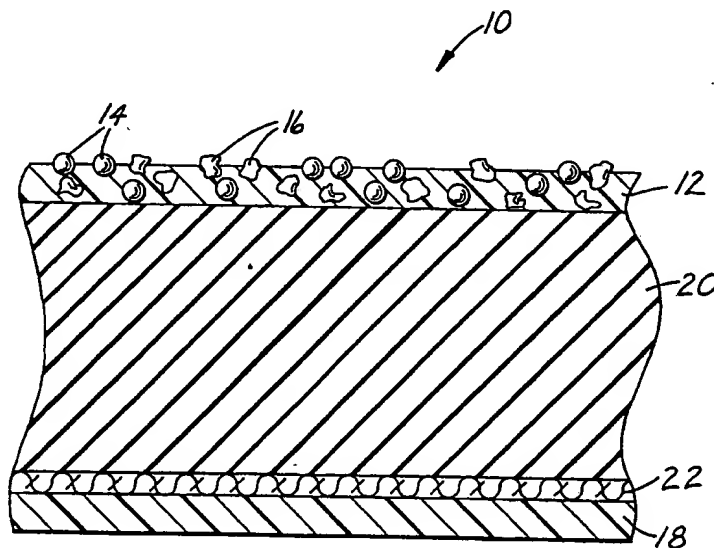
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 (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).  
 (72) Inventors: RICE, Eric, E. ; KLAMETH, Elmar, P., J. ; KEECH, Robert, L. ; PASSARINO, Sergio ; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: JORDAN, Robert, H. et al.; Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

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(54) Title: PAVEMENT MARKING TAPE



## (57) Abstract

Pavement marking tape which is yellow or orange in color and has a top layer, optional conformance layer, optional reinforcing web, and optional adhesive layer wherein said conformance layer is disposed between the top layer and the adhesive layer and which is substantially free of lead, cadmium, and chromium.

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PAVEMENT MARKING TAPEField of Invention

The present invention relates to yellow and  
5 orange pavement marking tapes which are substantially  
free of pigments containing lead, cadmium, or chromium.

Background

Colored pavement marking tapes are well known,  
10 being used in both long term, "permanent", and short  
term, "temporary" applications. Ease of application  
and customizable adhesive performance have led to the  
wide acceptance of such tapes for providing lane  
markings and other graphic information on road surfaces  
15 instead of such alternatives as paints.

Pavement marking tapes are typically made in  
desired colors by incorporation of pigments in the top  
layers thereof. Many colors, including especially  
yellow and orange, are achieved by incorporation of  
20 pigments containing lead, cadmium, and/or chromium.  
Such pigments can impart vivid, consistent, durable  
color, thereby enhancing the safety of the marking  
tapes in which they are used. In recent years,  
however, compounds including pigments containing lead,  
25 cadmium, and/or chromium have been the focus of  
increased concern over environmental and health risks.

Thus, there exists a need for alternative  
compounds for imparting desired coloration to pavement  
marking tapes.

30

Other Background

U.S. Patent Nos. 3,891,451 and 3,998,645  
(Okazaki et al.) disclose the use of Colour Index  
("C.I.") Pigment Yellow 83 in thermoplastic traffic  
35 paints.

Summary of Invention

The present invention provides yellow and  
orange pavement marking tapes which are free of lead,

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cadmium, and chromium. The tapes may be made in embodiments suitable for long term (i.e., "permanent") applications or short term (i.e., "temporary") applications.

5 In brief summary, a pavement marking tape of the invention comprises a top layer and an optional adhesive layer wherein the top layer is yellow or orange, comprises one or more pigments in a polymeric matrix, and the pigments are substantially free of  
10 lead, cadmium, and chromium. The top layer may comprise titanium dioxide, retroreflective elements, and/or anti-skid particles. Typically, the tape further comprises a conformance layer disposed between the top layer and the adhesive layer. In some  
15 embodiments, the tape may further comprise a reinforcing web.

#### Brief Description of Drawing

The invention will be further explained with  
20 reference to the drawing, wherein:

Figure 1 is cross-sectional view of an illustrative embodiment of pavement marking tape of the invention.

This figure, which is idealized, is not to  
25 scale and is intended to be merely illustrative and non-limiting.

#### Detailed Description of Illustrative Embodiments

As shown in Figure 1, in an illustrative  
30 embodiment of the invention, pavement marking tape 10 comprises top layer 12 and optional adhesive layer 18 on the bottom side thereof. Top layer 12 contains optional retroreflective elements 14 and optional anti-skid particles 16. Tape 10 also comprises  
35 optional conformance layer 20 and optional reinforcing web 22.

Top layer 12 is a polymeric matrix, e.g., of polyvinyl chloride ("PVC"), polyvinyl acetate ("PVA"), PVC/PVA blends, ethylene/acrylic acid ("EAA"),

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ethylene/methacrylic acid ("EMMA"), and EAA/EMAA blends, polyurethane, epoxy resins, melamine resins, or polyamides, that preferably exhibits tough, durable characteristics. Top layer 12 contains colorants to impart desired color thereto and, if desired, retroreflective elements 14 and/or anti-skid particles 16. Polyurethane-based top layers are typically preferred because such top layers are generally more durable than polyvinyl top layers. Polyurethane-based top layers have been used in pavement marking tapes for some time in view of their typically high tensile strength, tear strength, and abrasion resistance. In particular, aliphatic polyurethane resins exhibit superior abrasion resistance and color stability. Phenolic modified resins and aromatic urethanes that tend to discolor so as to turn brown may be less suitable than those that tend to turn yellow.

Top layer 12 contains an organic pigment or combination of two or more such pigments formulated to impart a desirable yellow or orange color to the pavement marking tape. By selection of particular pigments and adjusting the relative amounts which used, pavement markings may be made in desired colors, e.g., to satisfy applicable government specifications. In accordance with the invention, top layer 12 is substantially free of lead-, cadmium-, and chromium-containing pigments. Preferably, top layer 12 is substantially free of lead, cadmium, and chromium.

Illustrative examples of pigments which are suitable colorants for use in the invention include such yellow pigments such as:

- 1) Colour Index ("C.I.") Pigment Yellow 53 (e.g., HEUCOTECH<sup>TM</sup> HD156),
- 2) C.I. Pigment Yellow 55 (e.g., IRGALITE Brand Yellow BAF from Ciba-Geigy, a diarylide-p-toluidide),
- 3) C.I. Pigment Yellow 61 (e.g., WSC from Ciba-Geigy),

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- 4) C.I. Pigment Yellow 65 (e.g., DALAMAR Brand Yellow YT-820-D from Cookson Pigments Company, a monoazo),
  - 5) C.I. Pigment Yellow 74 (e.g., DALAMAR Brand Yellow YT-808-D from Cookson, a monoazo),
  - 6) C.I. Pigment Yellow 83 (e.g., DIAZO HR Brand from Hoechst),
  - 7) C.I. Pigment Yellow 110 (e.g., IRGAZINE Brand Yellow 3RLTN from Ciba-Geigy, a tetrachloroisindolinone),
  - 8) C.I. Pigment Yellow 138,
  - 9) C.I. Pigment Yellow 139 (e.g., Y5700 from Mobay),
  - 10) C.I. Pigment Yellow 184 (e.g., 10652 IRGACOLOR<sup>TM</sup> Yellow Bismuth Vanadium Oxide from Ciba Geigy),
  - 11) C.I. Pigment Yellow 191, and
  - 12) DALAMAR<sup>TM</sup> Yellow YT719, a monoazo from Cookson;
- such orange pigments as:
- 1) C.I. Pigment Orange 5 (e.g., IRGALITE Brand Red 2GW from Ciba-Geigy, a dinitraniline),
  - 2) C.I. Pigment Orange 13 (e.g., IRGALITE Brand Orange P from Ciba-Geigy, a diasopyrazolone),
  - 3) C.I. Pigment Orange 34 (e.g., IRGALITE Brand Orange F2G from Ciba-Geigy, a diasopyrazolone), and
  - 4) C.I. Orange 65 (e.g., IRGAZIN<sup>TM</sup> Orange 5R, a bis-azomethine nickel complex from Ciba-Geigy);
- and such red and violet pigments (which are useful in forming orange top coats) as:
- 1) C.I. Pigment Red 3 (e.g., IRGALITE<sup>TM</sup> Scarlet RNP and IRGALITE<sup>TM</sup> Red PDS4, both toluidene red from Ciba-Geigy),
  - 2) C.I. Pigment Red 4 (e.g., IRGALITE<sup>TM</sup> Red PRR a chlorinated para red from Ciba-Geigy),
  - 3) C.I. Pigment Red 48:3 (e.g., IRGALITE<sup>TM</sup> Red 2YB from Ciba-Geigy),
  - 4) C.I. Pigment Red 112 (e.g., IRGALITE<sup>TM</sup> Red 3RS, a BON arylamide from Ciba-Geigy),
  - 5) C.I. Pigment Red 144 (e.g., CROMOPHTAL<sup>TM</sup> Red BRN, an azocondensate from Ciba-Geigy),

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- 6) C.I. Pigment Red 166 (e.g., CROMOPHTAL Scarlet RN from Ciba-Geigy, an azocondensate),
- 7) C.I. Pigment Red 177 (e.g., CROMOPHTAL<sup>TM</sup> Red A2B, an anthraquinoid from Ciba-Geigy),
- 5 8) C.I. Pigment Red 207 (e.g., CINQUASIA<sup>TM</sup> Scarlet RT-787-D, a quinacridone from Ciba-Geigy), and
- 9) C.I. Pigment Violet 19 (e.g., CINQUASIA<sup>TM</sup> Red Y RT-759-D from Ciba-Geigy).

Top layer 12 of a pavement marking tape of the  
10 invention typically comprise between about 1.0 and about 20 weight percent of such organic pigment(s).

If desired, two or more pigments may be used in blends, some available commercially, to achieve desired top coat coloration. For example, HEUCOSIN<sup>TM</sup> G7633 and  
15 G7635, blends of C.I. Pigment Yellow 53, 138, and 191, from Cookson have been found to impart desirable yellow color to urethane-based top layers. In another illustrative example, a blend containing C.I. Pigment Yellow 53 (HEUCOTECH<sup>TM</sup> HD156), C.I. Pigment Yellow 61  
20 (WSC), and C.I. Pigment Yellow 139 (Y5700), in a 50.0:38.1:11.9 weight ratio was found to provide excellent nighttime yellow color in vinyl-based top layers having colorless microspheres.

The pigment(s) and polymer are preferably  
25 selected to be compatible with one another. They are preferably substantially non-reactive with one another. For instance, an acidic polymer and basic pigment may produce a composition too highly viscous to be easily worked. Furthermore, reaction between pigment(s) and  
30 polymer may result in undesirable change in resultant color. For example, C.I. Pigment Yellow 83 has been found to be substantially non-reactive with urethane polymers and is thus preferred for use in pavement markings made of such polymeric matrices.

35 In addition, top layer 12 typically contains titanium dioxide pigment which increases the CAP Y of the top layer as well as being useful in blending with yellow or orange pigments to achieve desired color. Also, in embodiments where, as discussed below,



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transparent glass microspheres 14 are to be incorporated into top layer 12 to impart retroreflective characteristics thereto, titanium dioxide renders top layer 12 opaque, increasing the retroreflective brightness of the microsphere 14. Top layer 12 typically comprises up to about 30 weight percent of titanium dioxide, with between about 5 and about 30 weight percent being preferred. Rutile titanium dioxide, urethane grade, is typically a suitable grade.

Top layer 12 is typically formed by coating a liquid composition of the various components and drying and/or curing the composition to yield top layer 12. Excessive amounts of titanium dioxide and pigment have been observed to undesirably increase the viscosity of the coating composition from which top layer 12 is formed.

In instances where the polymeric matrix is a two component polyurethane, e.g., the reaction product of one or more polyols and one or more isocyanates, the pigment is preferably dispersed in the polyol prior to mixing with the isocyanate component. This procedure is useful to reduce the likelihood of undesirable interaction between the pigment and the isocyanate or catalyst components which occurs in some instances, interfering with the reaction kinetics and impairing the color appearance of the resultant top layer.

Top layer 12 typically contains retroreflective elements 14 to impart improved nighttime visibility to the marking tape. As will be understood by those with ordinary skill in the art, retroreflective elements 14 are typically scattered throughout top layer 12 and may be partially embedded in top layer 12, protruding from the top surface thereof, and some may be totally embedded therein, becoming exposed as the top layer is progressively eroded away in use. Several suitable methods and formats of distribution of retroreflective elements are disclosed in U.S. Patent Nos. 4,279,534,

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4,322,177, 4,369,001, 4,607,978, 4,652,172, and  
4,681,480 (all Eigenmann).

Several suitable retroreflective elements are known and may be readily selected by those with  
5 ordinary skill in the art. One well-known type is microspheres, typically made of glass, which may be used bare or may have hemispheric reflectors, e.g., aluminum vapor coat, thereon. In the case of bare  
10 microspheres, pigment particles such as titanium dioxide in top layer 12 enhance retroreflective brightness. Microspheres with indexes of refraction of between about 1.5 and about 2.0 will provide efficient retroreflection under dry conditions and microspheres with indexes of refraction of between about 2.0 and  
15 about 2.2 provide efficient retroreflection under wet conditions. Accordingly, top layer 12 may comprise a mixture of microspheres selected from both ranges. In addition to microspheres, other suitable retroreflective elements include so-called cube-corner  
20 reflectors, etc.

It has been observed that although pavement markings of the invention exhibit good daytime color, they may tend to appear somewhat white or washed out at night, particularly at long distances corresponding to  
25 low observation angles. Accordingly, for some applications it is desirable to incorporate suitably colored microspheres in the marking. For instance, U.S. Patent No. 3,294,559 (Searight et al.) discloses yellow glass beads or microspheres which may be used in  
30 marking tapes of the invention. Other suitable colored microspheres will be apparent to those skilled in the art.

Typically, colorless microspheres provide brighter retroreflection than do colored microspheres.  
35 The aforementioned blend of C.I. Pigment Yellow 53, 61, and 139 has been observed to be particularly effective at imparting yellow daytime and nighttime color to pavement markings. It is believed that this blend of pigments contains a particularly suited combination of

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particle sizes to provide good light scattering properties so as to provide effective retroreflection and color.

Top layer 12 typically contains anti-skid particles 16 to improve the tire traction on the marking material. Anti-skid particles 16 are typically irregular or angular particles of sand, quartz, corundum, beryllium, silicon carbide, or other abrasive materials. Preferably anti-skid particles 16 exhibit a hardness of at least about 6° on the Mohs Hardness Scale, more preferably at least about 7°. Typically, average dimension of each anti-skid particle is between about 0.1 and about 1.0 millimeters, preferably between about 0.5 and about 0.8 millimeters.

Typically, it is preferred that the number of anti-skid particles in a given volume of top layer 12 is limited such that not more than 20 percent of the top surface of top layer 12 is covered by such particles, preferably between about 5 and 10 percent.

It may be desired to treat retroreflective elements 14 and anti-skid particles 16 with adhesion promoting agents or to incorporate such agents into top layer 12 to improve the bond with the polymeric matrix of top layer 12. Such agents typically have an inorganic moiety which associates with the retroreflective elements or anti-skid particles and an organic moiety which associates or reacts with the polymeric matrix.

Typically, pavement marking tape 10 will also comprise conformance layer 20 disposed between top layer 12 and adhesive layer 18. A typical conformance layer is made of highly filled acrylonitrile butadiene rubber or nitrile, properly filled (e.g., with mineral fillers) to provide desired physical properties such as suitable tensile strength, elongation, and conformability. Other illustrative examples of suitable materials include chloroprene (e.g., NEOPRENE<sup>TM</sup>) and chlorosulphonated polyethylene (e.g., HYPALON<sup>TM</sup>) which are well known for superior weathering

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and oil resistance. Conformance layer 20 may comprise up to 15 weight percent, typically about 1 to 12 weight percent, of organic or inorganic pigments (e.g., iron oxide, bismuth vanadate, titanium yellow, etc.) to provide better color matching with the top layer.

Optional adhesive layer 18, which adheres tape 10 to the pavement surface (not shown), is selected to provide desired adhesion properties. For instance, tape 10 may be intended for long term applications and should thus provide high durability. In instances where tape 10 is to be applied on a temporary basis, adhesive 18 should provide suitable release characteristics. In many instances, it is desirable for adhesive layer 18 to be a pressure-sensitive adhesive to facilitate application of tape 10 to the pavement.

In some embodiments, the adhesive is not applied to the marking tape until the time the tape is being applied to the pavement. For instance, colored top layers of the invention may be coated on the back or under side with contact cement just before application to the pavement, upon which contact cement is also typically preapplied. If desired, preformed strips of adhesive may be used to secure adhesive-less tapes of the invention.

In some embodiments, pavement marking tape 10 further comprises optional reinforcing web 22. Such a web is incorporated into the tape construction to increase the tensile strength and tear resistance of the tape. Such webs are especially preferred in instances where the tape is intended to be removed after use for a desired term as they facilitate removal of the tape which might otherwise tend to tear or shred upon application of a peel force. When used for such purposes, reinforcing web 12 is typically disposed at the interface of the adhesive layer and adjacent elements of tape 10 or within the adhesive layer itself.

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- Reinforcing web 22 should be made of a tough, tear resistant material with high tensile strength, e.g., polyester. Web 22 is typically in the form of an open weave or perforated sheet, preferably of
- 5 multifilament construction, or a fibrous, non-woven web, such that bulk of the layer(s) it is in, e.g., adhesive layer 18 and/or conformance layer 20, will flow through web 22, forming a strong bond thereto so as to reduce the potential for delamination failure.
- 10 It may be desirable to treat reinforcing web 22 with adhesion promoting agents, or incorporate such agents in the layers to improve the bond therebetween. U.S. Patent No. Re. 31,669 (Eigenmann), Great Britain Patent No. 2,085,056 (Eigenmann), and European Patent
- 15 Application Publications Nos. 162,229 (Eigenmann) and 304,405 (Mueller) disclose pavement marking tapes with reinforcing webs therein. Many suitable embodiments of reinforcing webs will be apparent to those skilled in the art.
- 20 Generally, pavement marking tapes of the invention will comprise a top layer between about 50 and about 300 microns, typically about 100 microns thick, a conformance layer between about 300 and 1200 microns, typically about 700 microns thick, and an
- 25 adhesive layer between about 50 and about 300, typically about 100 microns thick.

#### Examples

- The invention will be further explained by the
- 30 following illustrative examples which are intended to be nonlimiting. Unless otherwise indicated, all amounts are expressed in parts by weight.

- The daytime appearance of some members is expressed in C.I.E. color scale by the three
- 35 coordinates: x, y, and Cap Y, as determined in accordance with ASTM 1164-91 using a Hunter LABSCAN<sup>TM</sup> 2 LS-6000 Spectrocolorimeter.

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Example 1

A pavement marking was made with a yellow top layer comprising:

	<u>Amount</u>	<u>Component</u>
5	18.0	Titanium dioxide
	6.6	Yellow pigment (DIAZO HR Brand from Hoechst, C.I. Yellow 83)
	75.4	Polyurethane

The top layer, which was 100 microns thick after removal of solvents, had a color appearance as follows:

$$x = 0.47$$

$$y = 0.456$$

$$Y = 58.0$$

15 The yellow pigment, which was predispersed in the polyol component, did not react undesirably with the isocyanate component or the catalyst.

The conformance layer was 700 microns in thickness and comprised:

20	<u>Amount</u>	<u>Component</u>
	7.4	Nitrile rubber (BREON <sup>TM</sup> 3325, a 33% ACN from Zeon Corporation)
	7.0	Nitrile rubber (PERBUNAN <sup>TM</sup> 1807, an 18% ACN from Bayer)
25	1.9	SBS rubber (EUROPRENE SOL 161, from Enichem)
	2.0	Polyether (DYNAPOL <sup>TM</sup> 6206 from Huls)
30	11.0	Chloroparafin (CLOPARIN <sup>TM</sup> 70, 70% Cl from Caffare)
	2.0	Chloroparafin (CLOPARIN <sup>TM</sup> 68, 68% Cl from Caffare)
	6.2	Titanium dioxide (Anatase titanium dioxide from Bayer)
35	10.0	Amorphous silica (VULCASIL <sup>TM</sup> S from Bayer)

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- 20.0 Calcium silicate (VULCASIL™ G from Bayer)
- 0.4 Antioxidant (ANEX T, a phenyl antioxidant from
- 5 30.0 Glass beads (1.5 refractive index, 100 to 200 microns in diameter)
- 1.0 Yellow pigment
- 0.03 Orange pigment
- 0.4 Stearic acid
- 10 The conformance layer had a color appearance as follows:
- $x = 0.49$
- $y = 0.45$
- $Y = 54.1.$

15

Example 2

A pavement marking was made with a yellow top layer comprising:

	<u>Amount</u>	<u>Component</u>
20	12.0	Titanium dioxide
	10.0	Yellow pigment (DIAZO HR from Hoechst, Yellow 83)
	78.0	Polyurethane

- 25 The top layer, which was 100 microns thick after removal of solvents, had a color appearance as follows:

$$x = 0.4966$$

$$y = 0.4494$$

- 30  $Y = 50.71$

The conformance layer was a 700 micron thick layer like that used in Example 1.

Example 3

- 35 A pavement marking was made with a top layer comprising:

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	<u>Amount</u>	<u>Component</u>
	5.6	Titanium dioxide
	0.2	Yellow pigment (IRGAZIN Brand Yellow 3RLTN from Ciba-Geigy, C.I. Yellow 110)
5	4.8	Yellow pigment (IRGALITE Brand Yellow BAF from Ciba-Geigy, C.I. Yellow 55)
	8.5	Talc (MISTRON SUPERFROST from Cyprus Industrial Mineral Corp.)
	80.9	Polyurethane
10	The top layer, which was 100 microns thick after removal of solvents, had a color appearance as follows:	
	x = 0.473	
	y = 0.461	
15	Y = 60.0	
	The yellow pigment, which was predispersed in the polyols, reacted with the catalyst reducing the speed of cure. Complete curing was not achieved. It is believed that a continuous production process, with	
20	in-line addition of catalyst such as would be commonly be used in commercial production facility, would overcome this problem. Also, the top layer appeared to be slightly transparent and a somewhat reduced retroreflectivity (i.e., about 300	
25	millicandela/lux/meter <sup>2</sup> ) was noted.	

Example 4

A pavement marking was made with an orange top layer comprising:

	<u>Amount</u>	<u>Component</u>
30	12.3	Titanium dioxide
	6.7	Yellow pigment (DIAZO HR Yellow 83)
	1.2	Red Pigment (CROMOPHTAL Red 166 from Ciba-Geigy)
35	79.8	Polyurethane

The conformance layer was 700 microns in thickness, with similar composition as that in Example 1, except 1.0 parts by weight of C.I. Pigment Orange 34 was the only pigment used.



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Example 5

A pavement marking was made with a yellow top layer comprising:

	<u>Amount</u>	<u>Component</u>
5	2.2	Yellow pigment (Y5700 from Mobay, C.I. Pigment Yellow 139)
	7.1	Yellow pigment (WSC from Ciba-Geigy, C.I. Pigment Yellow 61)
	9.3	Yellow pigment (HEUCOTECH <sup>TM</sup> HD 156, C.I. Pigment Yellow 53)
10	81.5	Vinyl resin and plasticizer

The resultant top layer had a color appearance as follows:

	x = 0.5135
15	y = 0.4631
	Y = 51.16

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

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## Claims:

1. A pavement marking tape comprising a top layer and an adhesive layer wherein said top layer is yellow or orange, comprises one or more pigments in a polymeric matrix, and said pigments are substantially free of lead, cadmium, and chromium.
2. The tape of claim 1 wherein said top layer contains at least one of the following pigments: C.I. Pigment Yellow 53, C.I. Pigment Yellow 55, C.I. Pigment Yellow 61, C.I. Pigment Yellow 65, C.I. Pigment Yellow 74, C.I. Pigment Yellow 83, C.I. Pigment Yellow 110, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 184, C.I. Pigment Yellow 191, C.I. Pigment Orange 5, C.I. Pigment Orange 13, C.I. Pigment Orange 34, C.I. Pigment Orange 65, C.I. Pigment Red 3, C.I. Pigment Red 4, C.I. Pigment Red 48:3, C.I. Pigment Red 112, C.I. Pigment Red 144, C.I. Pigment Red 166, C.I. Pigment Red 177, C.I. Pigment Red 207, and C.I. Pigment Violet 19.
3. The tape of claim 1 wherein said top layer contains a blend of C.I. Pigment Yellow 53, C.I. Pigment Yellow 138, and C.I. Pigment yellow 191 in a urethane matrix.
4. The tape of claim 1 wherein said top layer contains a blend of C.I. Pigment Yellow 53, C.I. Pigment Yellow 61, and C.I. Pigment Yellow 139 in a vinyl matrix.
5. The tape of claim 1 wherein said polymeric matrix is polyvinyl or polyurethane.
6. The tape of claim 1 wherein said top layer comprises 1.0 to 20 weight percent of said pigment.

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7. The tape of claim 1 wherein said top layer comprises up to about 30 weight percent of titanium dioxide.

5           8. The tape of claim 1 further comprising a conformance layer disposed between said top layer and said adhesive layer.

9. The tape of claim 8 wherein said conformance  
10 layer comprises acrylonitrile butadiene rubber.

10. The tape of claim 8 wherein said conformance layer further comprises one or more organic pigments or inorganic pigments.

15           11. The tape of claim 8 wherein said top layer is about 100 microns thick, said conformance layer is about 700 microns thick, and said adhesive layer is about 100 microns thick.

20           12. The tape of claim 1 wherein said adhesive layer is a pressure-sensitive adhesive.

13. The tape of claim 1 wherein said top layer  
25 further comprises at least one of the following: retroreflective elements and anti-skid particles.

14. The tape of claim 1 further comprising reinforcing web.

30           15. The tape of claim 14 wherein said web is disposed at the interface of said adhesive layer and the other elements of said tape.

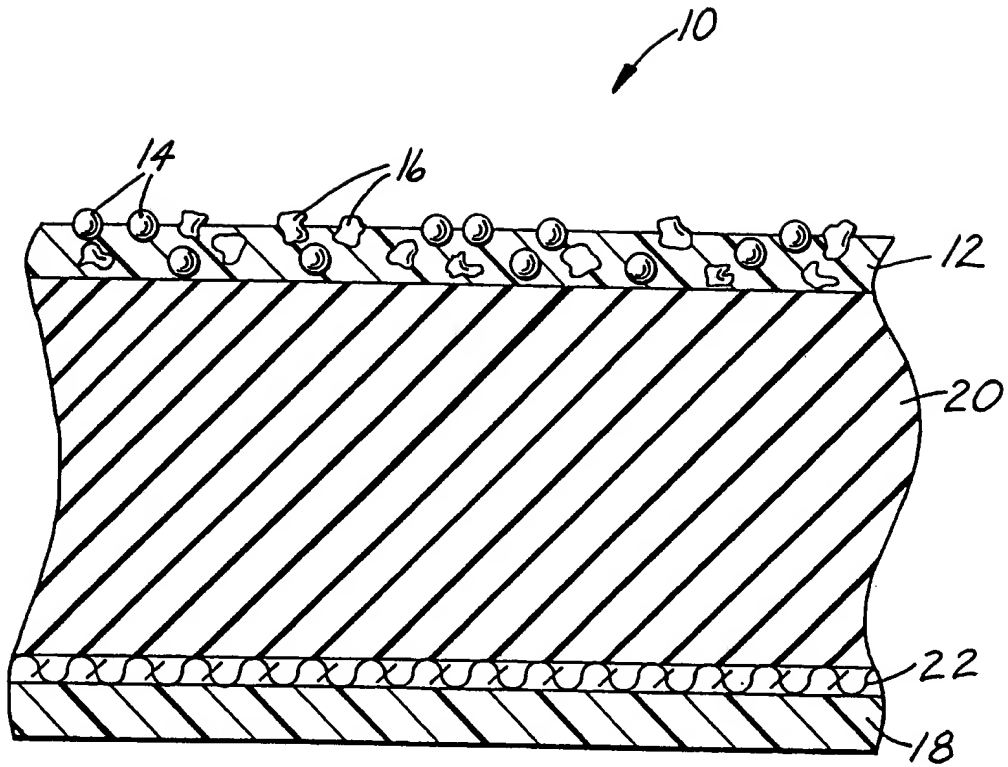
35           16. The tape of claim 14 wherein said web comprises at least one of the following: polyester, polyamide, polypropylene, or polyethylene.

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17. The tape of claim 1 wherein said tape is substantially free of lead, cadmium, or chromium.

18. A pavement marking tape which is yellow or  
5 orange in color, comprises one or more pigments,  
retroreflective elements, and anti-skid particles in a  
polymeric matrix wherein said tape is substantially  
free of lead, cadmium, or chromium.

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/00062

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 E01F9/08; E01F9/04		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	E01F ; C09J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US,A,3 337 483 (C.E. SEARIGHT ET AL) 22 August 1967	1-7, 12, 13, 17, 18
Y	see column 4, line 1-2; claims; example 3 ---	14-16
Y	EP,A,0 304 405 (SNOLINE S.P.A.) 22 February 1989 cited in the application see the whole document ---	14-16
Y	US,E,31 669 (EIGENMANN) 11 September 1984 cited in the application see claims ---  -/--	14-16
<p><sup>10</sup> Special categories of cited documents :<sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
11 MARCH 1993	30. 03. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DE JONGE S.J.P.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>DATABASE WPI Week 0580, Derwent Publications Ltd., London, GB; AN 80-08419C &amp; JP,A,54 160 433 (SEKISUI JUSHI KK) 19 December 1979 see abstract</p> <p>-----</p>	1-4

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9300062  
SA 68894

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

11/03/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3337483		None	
EP-A-0304405	22-02-89	None	
US-E-31669	11-09-84	DE-A, C 2716827	27-10-77
		GB-A- 1567527	14-05-80
		US-A- 4146635	27-03-79
		CA-A- 1044062	12-12-78
		JP-A- 52146031	05-12-77
		SE-B- 433236	14-05-84
		SE-A- 7704216	16-10-77